Classical and quantum approach to Davydov's soliton theory

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A method introduced by Davydov for modeling energy transport in deformable molecular chains is considered, using for the ansatz function a superposition of tensor products of single-exciton and coherent-phonon states. Treating the time-dependent parameters of the function (exciton and phonon amplitudes) as generalized coordinates, we have shown that the corresponding Euler-Lagrange equations are consistent with the averaged quantum equations, although the ansatz function does not satisfy the Schrödinger equation. For the case of the immobile-exciton limit (in which the quantum-mechanical problem is exactly solvable), it is shown that the ansatz function satisfies the Schrödinger equation, so all predictions based on Davydov's method are identical to the corresponding exact results (for this particular case).

I. INTRODUCTION

The understanding of the mechanisms of energy transport in molecular chains is of great importance, particularly from the point of view of bioenergetics; therefore great attention has been paid to the problem since the middle of the 1950s.[1,2] The idea about the soliton mechanism of the energy transport along the one-dimensional molecular chain, launched first by Davydov and Kislukha[3] in the 1970s is surely among the most interesting ones, but there still exists a controversy in the current scientific literature concerning its validity. Davydov with his collaborators, has elaborated this idea in many papers (see for example monography, cited as Ref. 4), and so did A. C. Scott with his team.[5] During the last three years, there appeared also articles indicating the limits of the applicability of this idea,[6–8] while Kerr and Lomdahl[9] have presented a quantum-mechanical derivation of the equation of motion for Davydov solitons, starting from the assumption that Davydov trial function ("Davydov's ansatz") satisfies Schrödinger's equation (SE). This problem was further treated in an exchange of comments by us[10] and Brown *et al.*[11] We wish to present here a more consistent approach based on Lagrangian formalism. We start with the brief summary of essential ingredients.

Davydov's initial point is Fröhlich's Hamiltonian,[1] where interaction energy between intramolecular excitations (Frenkel excitons) and harmonic chain vibrations is given within the linear approximation in phonon variables (molecular displacements). In the approximation of strong (or local) exciton-phonon coupling, the Hamiltonian takes the "standard" form (with ground-state energy already subtracted)

$$\hat{H}=\hat{H}_e+\hat{H}_{\rm ph}+\hat{H}_{\rm int}\ , \tag{1.1}$$

with

$$\hat{H}_e=\sum_n \Delta\hat{a}_n^\dagger\hat{a}_n - I\sum_n \hat{a}_n^\dagger(\hat{a}_{n+1}+\hat{a}_{n-1})\ , \tag{1.1a}$$

$$\hat{H}_{\rm ph}=\sum_q \hbar\omega_q\hat{b}_q^\dagger\hat{b}_q\ , \tag{1.1b}$$

$$\hat{H}_{\rm int}=\sum_{nq}\hbar\omega_q(\chi_n^q\hat{b}_q^\dagger+\chi_n^{*q}\hat{b}_q)\hat{a}_n^\dagger\hat{a}_n\ . \tag{1.1c}$$

Here $\hat{a}_n^\dagger$ and $\hat{a}_n$ are boson creation and annihilation operators, respectively, for quanta of intramolecular vibrations with energy Δ at site n; $\hat{b}_q^\dagger$ ($\hat{b}_q$) are creation (annihilation) operators for the phonon mode with energy $\hbar\omega_q$; and I is the intersite transfer energy produced by dipole-dipole interactions. The interaction coefficient χ_n^q has the following symmetry property: $\chi_n^{*q}=\chi_n^{-q}$, and in the nearest-neighbor approximation for the ordered chain, it can be written in the form

$$\chi_n^q=-2\chi i\left[\frac{\hbar}{2MN\omega_q}\right]^{1/2}\frac{\sin qa}{\hbar\omega_q}e^{-iqna}\equiv\chi_q e^{-iqna}\ ,$$

where a is the lattice constant, M is the mass of the molecule, and N is the number of molecules in the chain. The nonlinear coupling constant χ arises from modulation of the one-site energy by the molecular displacements.

The structure of the paper is as follows: Sec. II is devoted to the study of quantum (Schrödinger's and Heisenberg's) equations of motion while Sec. III introduces Lagrange's (and Hamilton's) equations. In Sec. IV we discuss the internal self-consistency of the total system of equations (validity of the Schrödinger equation) and the Sec. V presents a detailed study of the particular case of the immobile-exciton limit ($I=0$). The paper closes with a concise conclusion.

II. QUANTUM EQUATIONS OF MOTION

Brown *et al.*[12] have indicated that Davydov's simple trial function in the form of a tensor product of exciton and phonon function cannot be the solution of Schrödinger's equation for the Hamiltonian with interaction; therefore, following their works,[7,8] we study the trial function which is the linear combination of tensor products (in fact, which also was first introduced by Davydov[13]):

$$|D_1(t)\rangle=\sum_n\psi_n(t)\hat{a}_n^\dagger|0\rangle_{\rm ex}|\beta_n(t)\rangle\ , \tag{2.1}$$

where

$$|\beta_n(t)\rangle=e^{-\hat{S}_n(t)}|0\rangle_{\rm ph}$$
$$=\exp\left[-\sum_q(\beta_{nq}^*(t)\hat{b}_q-\beta_{nq}(t)\hat{b}_q^\dagger)\right]|0\rangle_{\rm ph}$$

are Glauber coherent phonon states, which satisfy the following orthogonality relation:

$$\langle \beta'_n | \beta_m \rangle = \exp\left[-\tfrac{1}{2} \sum_q (|\beta_{nq} - \beta_{mq}|^2 + \beta^*_{mq}\beta_{nq} - \beta_{mq}\beta^*_{nq}) \right] . \tag{2.1a}$$

The next step is the *assumption* that $|D_1(t)\rangle$ satisfies Schrödinger's equation with the Hamiltonian (1.1):

$$i\hbar \frac{\partial}{\partial t} |D_1(t)\rangle = \hat{H} |D_1(t)\rangle . \tag{2.2}$$

The explicit calculation gives

$$\sum_m \Bigg[\Bigg\{ i\hbar\dot{\psi}_m(t) + \frac{i\hbar}{2} \sum_q \psi_m^{(t)} [\dot{\beta}_{mq}(t)\beta^*_{mq}(t) - \dot{\beta}^*_{mq}(t)\beta_{mq}(t)] - \Delta\psi_m(t)$$
$$- \psi_m(t) \sum_q \hbar\omega_q [\chi^q_m \beta^*_{mq}(t) + \chi^{*q}_m \beta_{mq}(t) + |\beta_{mq}(t)|^2] \Bigg\} |\beta_m(t)\rangle$$
$$+ I[\psi_{m+1}(t)|\beta_{m+1}(t)\rangle + \psi_{m-1}(t)|\beta_{m-1}(t)\rangle]$$
$$+ \sum_q \psi_m(t)[i\hbar\dot{\beta}_{mq}(t) - \hbar\omega_q(\beta_{mq}(t) + \chi^q_m)] e^{-\hat{S}_m(t)} \hat{b}^\dagger_q |0\rangle_{\rm ph} \Bigg] \hat{a}^\dagger_n |0\rangle_{\rm ex} = 0 . \tag{2.3}$$

In order to arrive at the differential equations for $\psi_m(t)$ and $\beta_{mq}(t)$ we shall project SE (2.3) onto some particular directions.

(a) Projection onto $|\beta_n\rangle \hat{a}^\dagger_n |0\rangle_{\rm ex}$ gives

$$i\hbar\dot{\psi}_n(t) = \Bigg\{ \Delta - \frac{i\hbar}{2} \sum_q [\dot{\beta}_{nq}(t)\beta^*_{nq}(t) - \dot{\beta}^*_{nq}(t)\beta_{nq}(t)] + \sum_q \hbar\omega_q [\chi^q_n \beta^*_{nq}(t) + \chi^{*q}_n \beta_{nq}(t) + |\beta_{nq}(t)|^2] \Bigg\} \psi_n^{(t)}$$
$$- I[\psi_{n+1}(t)\langle \beta_n(t)|\beta_{n+1}(t)\rangle + \psi_{n-1}\langle \beta_n(t)|\beta_{n-1}(t)\rangle] . \tag{2.4}$$

(b) Projection onto $\hat{a}^\dagger_n |0\rangle_{\rm ex} e^{-\hat{S}_n(t)} \hat{b}^\dagger_q |0\rangle_{\rm ph}$ gives

$$i\hbar\psi_n(t)\dot{\beta}_{nq}(t) = \hbar\omega_q \psi_n(t)[\beta_{nq}(t) + \chi^q_n] - I\{\psi_{n+1}(t)[\beta_{n+1q}(t) - \beta_{nq}(t)]\langle \beta_n(t)|\beta_{n+1}(t)\rangle$$
$$+ \psi_{n-1}(t)[\beta_{n-1q}(t) - \beta_{nq}(t)]\langle \beta_n(t)|\beta_{n-1}(t)\rangle\} , \tag{2.5}$$

while projecting (2.3) onto $|D_1(t)\rangle$ (averaging) gives

$$i\hbar \sum_n \dot{\psi}_n(t)\psi^*_n(t) + \frac{i\hbar}{2} \sum_{nq} |\psi_n(t)|^2 [\dot{\beta}_{nq}(t)\beta^*_{nq}(t) - \dot{\beta}^*_{nq}(t)\beta_{nq}(t)]$$
$$= \sum_n \Delta |\psi_n(t)|^2 - I \sum_n \psi^*_n(t)[\psi_{n+1}(t)\langle \beta_n|\beta_{n+1}\rangle + \psi_{n-1}(t)\langle \beta_n|\beta_{n-1}\rangle]$$
$$+ \sum_{nq} |\psi_n(t)|^2 [|\beta_{nq}(t)|^2 + \chi^{*q}_n \beta_{nq}(t) + \chi^q_n \beta^*_{nq}(t)] \equiv \langle D_1(t)|\hat{H}|D_1(t)\rangle . \tag{2.6}$$

One can easily show that the substitution of (2.4) into (2.6) leads to an identity, regardless of the form of $\dot{\beta}_{nq}(t)$.

The other possible approach is to study the equations of motion for the operators [Heisenberg equation (HE)]. We start with the HE for $\hat{b}_q(t)$:

$$i\hbar\dot{\hat{b}}_q(t) = \hbar\omega_q \hat{b}_q(t) + \sum_m \hbar\omega_q \chi^q_m \hat{a}^\dagger_m(t)\hat{a}_m(t) . \tag{2.7}$$

If SE is valid, then

$$i\hbar\langle D_1(0)|\dot{\hat{b}}_q(t)|D_1(0)\rangle = i\hbar\frac{\partial}{\partial t}\langle D_1(t)|\hat{b}_q|D_1(t)\rangle$$
$$= \langle D_1(t)|[\hat{b}_q, \hat{H}]|D_1(t)\rangle , \tag{2.8}$$

and using

$$\langle D_1(t)|\hat{b}_q|D_1(t)\rangle = \sum_n |\psi_n(t)|^2 \beta_{nq}(t) \tag{2.9}$$

we obtain

$$i\hbar\frac{\partial}{\partial t} \sum_n |\psi_n(t)|^2 \beta_{nq}(t)$$
$$= \sum_n \hbar\omega_q |\psi_n(t)|^2 (\beta_{nq}(t) + \chi^q_n) . \tag{2.10}$$

Now, writing HE for $\hat{a}^\dagger_m(n)\hat{a}_m(t)$ and averaging it over $|D_1(t)\rangle$ one gets

$$i\hbar\frac{\partial}{\partial t}|\psi_n(t)|^2 = -I[\psi^*_n(t)\psi_{n+1}(t)\langle \beta_n|\beta_{n+1}\rangle$$
$$+ \psi^*_n(t)\psi_{n-1}(t)\langle \beta_n|\beta_{n-1}\rangle$$
$$- \psi_n(t)\psi^*_{n+1}(t)\langle \beta_{n+1}(t)|\beta_n(t)\rangle$$
$$- \psi_n(t)\psi^*_{n-1}(t)\langle \beta_{n-1}(t)|\beta_n(t)\rangle] . \tag{2.11}$$

Combination of (2.10) and (2.11) gives

$$\sum_n \psi_n^*(t)\{i\hbar\psi_n(t)\dot\beta_{nq}(t)-\hbar\omega_q\psi_n(t)[\beta_{nq}(t)+\chi_n^q]\}$$
$$=-I\sum_n \psi_n^*(t)\{\psi_{n+1}(t)[\beta_{n+1q}(t)-\beta_{nq}(t)]\langle\beta_n|\beta_{n+1}\rangle+\psi_{n-1}(t)[\beta_{n-1q}(t)-\beta_{nq}(t)]\langle\beta_n|\beta_{n-1}\rangle\}\ , \tag{2.12}$$

and having in mind that there exists linear independent of $\{\psi_n^*\}$, the coefficients of ψ_n^* give

$$i\hbar\psi_n(t)\dot\beta_{nq}(t)=\hbar\omega_q\psi_n(t)[\beta_{nq}(t)+\chi_n^q]-I\{\psi_{n+1}(t)[\beta_{n+1q}(t)-\beta_{nq}(t)]\langle\beta_n|\beta_{n-1}\rangle$$
$$+\psi_{n-1}[\beta_{n-1q}(t)-\beta_{nq}(t)]\langle\beta_n|\beta_{n-1}\rangle\}\ , \tag{2.13}$$

which is precisely (2.5). Therefore, we have shown that, under the assumption that $|D_1(t)\rangle$ satisfies the SE, there is no inconsistency between averaged HE and SE, because they both lead to the same equations of motion for $\beta_{nq}(t)$ and $\psi_n(t)$. Of course, this is not yet the proof that $|D_1(t)\rangle$ does satisfy SE. In Sec. IV we shall try to answer this question.

III. LAGRANGIAN FORMALISM

Strict formulation of the Lagrangian formalism[14,15] starts from

$$L=\left\langle D_1(t)\left|\frac{i\hbar}{2}\frac{\overleftrightarrow{\partial}}{\partial t}-\hat H\right|D_1(t)\right\rangle=L_t-\mathcal{H}\ , \tag{3.1}$$

with

$$L_t=\frac{i\hbar}{2}\sum_n(\dot\psi_n\psi_n^*-\dot\psi_n^*\psi_n)$$
$$+\frac{i\hbar}{2}\sum_{nq}|\psi_n|^2(\dot\beta_{nq}\beta_{nq}^*-\dot\beta_{nq}^*\beta_{nq}) \tag{3.1a}$$

and

$$\mathcal{H}\equiv\langle D_1(t)|\hat H|D_1(t)\rangle=\sum_n\Delta|\psi_n|^2-I\sum_n\psi_n^*(\psi_{n+1}\langle\beta_n|\beta_{n+1}\rangle+\psi_{n-1}\langle\beta_n|\beta_{n-1}\rangle)$$
$$+\sum_{nq}|\psi_n|^2\hbar\omega_q(|\beta_{nq}|^2+\chi_n^q\beta_{nq}^*+\chi_n^{*q}\beta_{nq})\ , \tag{3.1b}$$

where $\mathcal{H}$ can be proven to be the classical Hamilton function. The Euler-Lagrange equation (ELE) for $\psi_n(t)$ is

$$i\hbar\dot\psi_n(t)+\frac{i\hbar}{2}\psi_n(t)\sum_q[\dot\beta_{nq}(t)\beta_{nq}^*(t)-\dot\beta_{nq}^*(t)\beta_{nq}(t)]$$
$$=\frac{\partial\mathcal{H}}{\partial\psi_n^*}=\Delta\psi_n-I(\psi_{n+1}\langle\beta_n|\beta_{n+1}\rangle+\psi_{n-1}\langle\beta_n|\beta_{n-1}\rangle)+\psi_n\sum_q\hbar\omega_q(|\beta_{nq}|^2+\chi_n^q\beta_{nq}^*+\chi_n^{*q}\beta_{nq}) \tag{3.2}$$

which agrees with (2.4). The ELE for the variable $\varphi_n\equiv\beta_{nq}$ (or β_{nq}^*):

$$\frac{d}{dt}\left[\frac{\partial L}{\partial\dot\varphi_n}\right]-\frac{\partial L}{\partial\varphi_n}=0$$

gives

$$\frac{i\hbar}{2}|\psi_n|^2\dot\beta_{nq}+\frac{i\hbar}{2}\frac{d}{dt}(|\psi_n|^2\beta_{nq})=\frac{\partial\mathcal{H}}{\partial\beta_{nq}^*}\ , \tag{3.3a}$$

$$-\frac{i\hbar}{2}|\psi_n|^2\dot\beta_{nq}^*-\frac{i\hbar}{2}\frac{d}{dt}(|\psi_n|^2\beta_{nq}^*)=\frac{\partial\mathcal{H}}{\partial\beta_{nq}}\ , \tag{3.3b}$$

where the problem is the evaluation of

$$\frac{\partial}{\partial\beta_{nq}}\langle\beta_n|\beta_{n\pm1}\rangle\quad\left[\text{or }\frac{\partial}{\partial\beta_{nq}^*}\langle\beta_n|\beta_{n\pm1}\rangle\right].$$

A tedious calculation [using (2.1a), (3.2), and (3.3a)] gives finally

$$i\hbar|\psi_n(t)|^2\dot\beta_{nq}(t)=\hbar\omega_q[\beta_{nq}(t)+\chi_n^q]|\psi_n(t)|^2$$
$$-I\psi_n^*(t)\{\psi_{n+1}(t)[\beta_{n+1q}(t)-\beta_{nq}(t)]\langle\beta_n|\beta_{n+1}\rangle+\psi_{n-1}(t)[\beta_{n-1q}(t)-\beta_{nq}(t)]\langle\beta_n|\beta_{n-1}\rangle\}\ . \tag{3.4}$$

Factor ψ_n^* can be canceled, and the remaining equation is just (2.5). Our conclusions can be formulated as follows.

(i) If one supposes that $|D_1(t)\rangle$ satisfies the SE, then the equations of motion for $\psi_n(t)$ and $\beta_{nq}(t)$ obtained by projecting the SE onto some particular directions, averaged HE's and ELE's obtained from the Lagrangian of the system, are completely equivalent.

(ii) The Hamilton equations for $\psi_n(t)$ and $\beta_{nq}(t)$ (which must be identical to ELE) cannot be obtained simply from

$$i\hbar\dot{\psi}_n=\frac{\partial\mathcal{H}}{\partial\psi_n^*},\quad i\hbar\dot{\beta}_{nq}=\frac{\partial\mathcal{H}}{\partial\beta_{nq}^*} \tag{3.5}$$

(as proposed by Davydov[13] and Brown *et al.*[7,8]), but must be obtained from Hamilton's principle in the form

$$\delta\int_{t_1}^{t_2}\left[\mathcal{H}-\sum_n\frac{\partial L}{\partial\dot{\varphi}_n}\dot{\varphi}_n\right]dt=0\ , \tag{3.6}$$

which, in this case, gives the same equations (3.2) and (3.3).

The nonapplicability of Eqs. (3.5) is the direct consequence of the fact that the Lagrangian (3.1) is a linear function of "generalized velocities" $\dot{\psi}_n(t)$ and $\dot{\beta}_{nq}(t)$, so the choice of the conjugated canonical (or Hamilton) variables is rather ambiguous.[16]

IV. EQUATION OF MOTION FOR THE FUNCTION $|D_1(t)\rangle$

Until now we have assumed that $|D_1(t)\rangle$ satisfies the SE, and all the equations for the time-dependent coefficients $\psi_n(t)$ and $\beta_{nq}(t)$ that followed from it were consistent. As we have already mentioned, this consistency is not the proof that $|D_1(t)\rangle$ does satisfy the SE. In fact, one must prove the self-consistency of the ELE [for $\psi_n(t)$ and $\beta_{nq}(t)$] and the SE for $|D_1(t)\rangle$; that is, substitution of $\dot{\psi}_n(t)$ and $\dot{\beta}_{nq}(t)$ from the ELE into the SE for $|D_1(t)\rangle$ (not projecting the SE into any direction) must result in an identity. If this statement is true, it means that the ELE's are the necessary and sufficient condition for the validity of the SE.

Following the above-mentioned scheme, we substitute the ELE [(2.4) and (2.5)] into the time derivative $i\hbar(\partial/\partial t)|D_1(t)\rangle$

$$\begin{aligned}i\hbar\frac{\partial}{\partial t}|D_1(t)\rangle=&\,i\hbar\sum_n\dot{\psi}_n(t)\hat{a}_n^\dagger|0\rangle_{\rm ex}|\beta_m(t)\rangle+\tfrac{1}{2}i\hbar\sum_{nq}\psi_n(t)[\dot{\beta}_{nq}(t)\beta_{nq}^*(t)-\dot{\beta}_{nq}^*(t)\beta_{nq}(t)]\hat{a}_n^\dagger|0\rangle_{\rm ex}|\alpha_n(t)\rangle\\&+i\hbar\sum_{nq}\psi_n(t)\beta_{nq}(t)e^{-\hat{S}_m(t)}\hat{b}_q|0\rangle_{\rm ph}\hat{a}_n^\dagger|0\rangle_{\rm ex}\ .\end{aligned} \tag{4.1}$$

After arranging the terms, we arrive to the following important result:

$$i\hbar\frac{\partial}{\partial t}|D_1(t)\rangle=\hat{H}|D_1(t)\rangle+|\delta(t)\rangle\ , \tag{4.2}$$

where

$$\begin{aligned}|\delta(t)\rangle=-I\sum_m\{&\psi_{m+1}(\langle\beta_m|\beta_{m+1}\rangle|\beta_m\rangle-|\beta_{m+1}\rangle)-\psi_{m-1}(\langle\beta_m|\beta_{m-1}\rangle|\beta_m\rangle-|\beta_{m-1}\rangle)\\&+\sum_q[\psi_{m+1}(\beta_{m+1q}-\beta_{mq})\langle\beta_m|\beta_{m+1}\rangle+\psi_{m-1}(\beta_{m-1q}-\beta_{mq})\langle\beta_m|\beta_{m-1}\rangle]\\&\times e^{-\hat{S}_m}\hat{b}_q^\dagger|0\rangle_{\rm ph}\}\hat{a}_m^\dagger|0\rangle_{\rm ex}\ ,\end{aligned} \tag{4.3}$$

which satisfies the orthogonality relation

$$\langle D_1(t)|\delta(t)\rangle=0\ . \tag{4.4}$$

Equation (4.2) is the crucial one, because it shows that when the ELE, obtained by projecting the SE, are substituted back into the SE, one is not led to an identity, but to the equation (4.2).

First of all one can notice that since $|\delta(t)\rangle$ is proportional to I, for the case of immobile excitation $I=0$, the function $|D_1(t)\rangle$ with coefficients, whose time dependence is defined by the ELE, satisfies the SE. This case will be discussed in detail in Sec. V.

Further on, projecting (4.2) onto the directions $|\beta_n\rangle a_n^\dagger|0\rangle_{\rm ex}$ and $e^{-\hat{S}_n(t)}\hat{b}_q^\dagger|0\rangle_{\rm ph}\hat{a}_n^\dagger|0\rangle_{\rm ex}$ (see Sec. III), we obtain the ELE's (2.4) and (2.5). Finally, the fact that $|D_1(t)\rangle$ is orthogonal to $|\delta(t)\rangle$ has an important consequence, that the averaged equation (4.2),

$$\begin{aligned}\left\langle D_1(t)\left|i\hbar\frac{\partial}{\partial t}\right|D_1(t)\right\rangle&=\langle D_1(t)|\hat{H}|D_1(t)\rangle+\langle D_1(t)|\delta(t)\rangle\\&\equiv\langle D_1(t)|\hat{H}|D_1(t)\rangle\ ,\end{aligned} \tag{4.5}$$

is completely consistent with all previously derived equations.

Let us now compare the energy of the system calculated with the wave function $|D_1(t)\rangle$, whose dynamics is determined by Eq. (4.2) [coefficients $\psi_n(t)$ and $\beta_{nq}(t)$ satisfy the ELE] and the (unknown) solution of the SE evolving from the same initial state $|D_1(0)\rangle$:

$$|\psi(t)\rangle=e^{-(i/\hbar)\hat{H}t}|D_1(0)\rangle\ . \tag{4.6}$$

It is clear that

$$\langle \psi(t)|\hat{H}|\psi(t)\rangle = \langle D_1(0)|\hat{H}|D_1(0)\rangle \equiv \mathcal{H}(t=0) \ . \quad (4.7)$$

It is easy to show [using (4.2)] that

$$\frac{d}{dt}\langle D_1(t)|\hat{H}|D_1(t)\rangle = \langle D_1(t)|\hat{H}|\delta(t)\rangle - \langle \delta(t)|\hat{H}|D_1(t)\rangle \ , \quad (4.8)$$

so that

$$\langle D_1(t)|\hat{H}|D_1(t)\rangle = \langle D_1(0)|\hat{H}|D_1(0)\rangle = \langle \psi(t)|\hat{H}|\psi(t)\rangle \ . \quad (4.9)$$

We see that the energy of the system is the same as that calculated with both functions. This fact, together with the above-mentioned consistency of the "classical" equations and the averaged SE, was probably the reason why the most of the authors, who previously dealt with this problem, never questioned the validity of the SE for the function $|D_1(t)\rangle$.

In fact, the additional $|\delta(t)\rangle$ term in (4.2) turns $|D_1(t)\rangle$ into an approximate solution of the SE, and we postpone the estimate of the influence of this approximation onto other average values and kinetic properties of the system until the second paper of this series.

V. CASE OF THE "IMMOBILE EXCITON"

This section will be devoted to the study of the limiting case of the "immobile exciton" $I=0$, where we shall compute some relevant quantities of the system starting from the ELE's and compare them with the corresponding solutions of the quantum equations, which, in this case, can be solved exactly as was shown by Brown *et al.*[8] (further on referred to as BWL).

The Fröhlich Hamiltonian (FH) (1.1) (with $I=0$) can be put into the diagonal form (see BWL) by unitary transformation with the operator

$$\hat{U} = \exp\left[-\sum_{nq}(\chi_n^q \hat{b}_q^\dagger - \chi_n^{*q}\hat{b}_q)\hat{a}_n^\dagger \hat{a}_n\right] \ . \quad (5.1)$$

"Dressed" operators are given by the expressions

$$\hat{A}_m = \hat{U}\hat{a}_m\hat{U}^\dagger = \hat{a}_m \exp\left[\sum_q(\chi_m^q \hat{b}_q^\dagger - \chi_m^{*q}\hat{b}_q)\right] \ , \quad (5.2a)$$

$$\hat{B}_q = \hat{U}\hat{b}_q\hat{U} = \hat{b}_q + \sum_m \chi_m^q \hat{a}_m^\dagger \hat{a}_m \ , \quad (5.2b)$$

while the transformed FH has the form

$$\hat{H} = -\sum_n |\chi_n^q|^2 \hat{A}_n^\dagger \hat{A}_n + \sum_q \hbar\omega_q \hat{B}_q^\dagger \hat{B}_q \ , \quad (5.3)$$

where terms with two-particle interaction were neglected because we shall hereafter study only single-particle exciton states.

Starting from the initial state in the form

$$|D_1(0)\rangle \equiv |\phi(0)\rangle = \sum_n \psi_n(0)\hat{a}_n^\dagger|0\rangle_{\text{ex}} \times \exp\left[\sum_q[\beta_{nq}(0)\hat{b}_q^\dagger - \beta_{nq}^*(0)\hat{b}_q]\right]|0\rangle_{\text{ph}} \ , \quad (5.4)$$

and defining the functions $|\phi_1(t)\rangle \equiv |D_1(t)\rangle$, where $\psi_n(t)$ and $\beta_{nq}(t)$ are solutions of the ELE [for the initial values $\psi_n(0)$ and $\beta_{nq}(0)$] and the exact solution of Schrödinger's equation

$$|\phi(t)\rangle = e^{-(i/\hbar)\hat{H}t}|\phi(0)\rangle \ , \quad (5.5)$$

we shall calculate the following quantities: (i)

$$\langle \phi_1(t)|\hat{U}_n|\phi_1(t)\rangle \ ,$$

where $\hat{U}_n$ is the phonon displacement; (ii)

$$\left\langle \phi_1(t)\left|\sum_q \hbar\omega_q \hat{b}_q^\dagger \hat{b}_q\right|\phi_1(t)\right\rangle$$

energy of phonon subsystem; (iii) the scalar product

$$\langle \phi_1(t)|\phi(t)\rangle$$

which gives the measure of the deviation of Davydov's state from the exact state vector $|\phi(t)\rangle$. Results of (i) and (ii) will be compared with the exact results

$$\langle \phi(t)|\hat{U}_n|\phi(t)\rangle$$

and

$$\langle \phi(t)|\hat{H}_{\text{ph}}|\phi(t)\rangle \ ,$$

which can be easily calculated for $I=0$.

Solving Heisenberg's equations of motion for $\hat{b}_q(t)$ (2.7) for $I=0$, we obtain

$$\hat{b}_q(t) = \hat{b}_q(0)e^{-i\omega_q t} - (1-e^{-i\omega_q t})\sum_m \chi_m^q \hat{a}_m^\dagger(0)\hat{a}_m(0) \quad (5.6)$$

and bearing in mind the relation

$$\langle \phi(t)|\hat{U}_n|\phi(t)\rangle = \langle \phi(0)|\hat{U}_n(t)|\phi(0)\rangle \ ,$$

expressing $\hat{U}_n$ in terms of $\hat{b}_q$ and $\hat{b}_q^\dagger$, we obtain

$$\langle \phi(t)|\hat{U}_n|\phi(t)\rangle = \sum_{mq}\left[\frac{\hbar}{2MN\omega_q}\right]^{1/2} e^{-iqna}[\beta_{mq}^*(0)e^{i\omega_q t} + \beta_{m,-q}(0)e^{-i\omega_q t}] - 2\sum_{mq}\left[\frac{\hbar}{2MN\omega_q}\right]^{1/2} e^{-iqna}\chi_m^{-q}P_m(1-\cos\omega_q t), \quad P_m \equiv |\psi_m(0)|^2 \ . \quad (5.7)$$

Similarly,

$$\left\langle \phi(t) \left| \sum_q \hbar\omega_q \hat{b}_q^\dagger \hat{b}_q \right| \phi(t) \right\rangle = \sum_{nq} \hbar\omega_q P_n |\beta_{nq}(0)e^{-i\omega_q t} - (1-e^{-i\omega_q t})\chi_m^q|^2 \ . \quad (5.8)$$

On the other hand, the ELE's for $\psi_n(t)$ (2.4) and $\beta_{nq}(t)$ (2.5), in the case $I=0$, take the form

$$i\hbar\dot{\psi}_n(t) = \Delta\psi_n(t) + \tfrac{1}{2}\psi_n(t)\sum_q \hbar\omega_q[\chi_n^q\beta_{nq}^*(t) + \chi_n^{*q}\beta_{nq}(t)] \ , \quad (5.9a)$$

where

$$i\hbar\dot{\beta}_{nq}(t) = \hbar\omega_q[\beta_{nq}(t) + \chi_n^q] \ . \quad (5.9b)$$

The solutions of (5.9), with initial values $\psi_n(0)$ and $\beta_{nq}(0)$ are

$$\beta_{nq}(t) = \beta_{nq}(0)e^{-i\omega_q t} - \chi_n^q(1-e^{-i\omega_q t}) \ , \quad (5.10a)$$

$$\psi_n(t) = \psi_n(0)e^{-i\lambda_n(t)} \ , \quad (5.10b)$$

where

$$\lambda_n(t) = \sum_q \{\mathrm{Im}[\chi_n^q\beta_{nq}^*(0)(e^{i\omega_q t}-1)] - \omega_q|\chi_n^q|^2 + |\chi_n^q|^2\sin\omega_q t\} \ . \quad (5.10c)$$

Now, using the solutions (5.10) one gets

$$\begin{aligned}\langle\phi_1(t)|\hat{U}_n|\phi_1(t)\rangle &= \sum_{mq}\left[\frac{\hbar}{2MN\omega_q}\right]^{1/2} e^{-iqna}P_m[\beta_{mq}^*(t) + \beta_{m,-q}(t)] \\ &= \sum_{mq}\left[\frac{\hbar}{2MN\omega_q}\right]^{1/2} e^{-iqna}P_m[\beta_{mq}^*(0)e^{i\omega_q t} + \beta_{m,-q}(0)e^{-i\omega_q t}] \\ &\quad - \sum_{mq}\left[\frac{\hbar}{2MN\omega_q}\right]^{1/2} e^{-iqna}P_m\chi_m^{-q}(1-\cos\omega_q t) \ , \end{aligned} \quad (5.11)$$

which is identical to (5.7). In the same way, we obtain the energy of the phonon subsystem

$$\left\langle \phi_1(t) \left| \sum_q \hbar\omega_q \hat{b}_q^\dagger \hat{b}_q \right| \phi_1(t) \right\rangle = \sum_{nq}\hbar\omega_q P_n|\beta_{nq}(t)|^2 = \sum_{nq}\hbar\omega_q P_n|\beta_{nq}(0)e^{-i\omega_q t} - (1-e^{-i\omega_q t})\chi_n^q|^2 \ . \quad (5.12)$$

This result also agrees with (5.8).

The scalar product $\langle\phi_1(t)|\phi(t)\rangle$ will be obtained by the procedure described in detail in the Appendix A of BWL, so we shall present here a brief description. We start with

$$\begin{aligned}\langle\phi_1(t)|\phi(t)\rangle &= \sum_{nm}\psi_m^*(t)\psi_n(0)\left\langle 0 \left| \left[\exp\left[-\sum_q[\beta_{mq}(t)\hat{b}_q^\dagger - \beta_m^*(t)\hat{b}_q]\right]\right.\right.\right. \\ &\qquad \left.\left.\left. \times\hat{a}_m e^{-(i/\hbar)\hat{H}t}\hat{a}_n^\dagger \exp\left[\sum_{q'}[\beta_{nq'}(0)\hat{b}_{q'}(0) - \beta_{nq'}^*(0)\hat{b}_{q'}(0)]\right]\right]\right| 0\right\rangle \\ &= \sum_{nm}\psi_m^*(t)\psi_n(0)\left\langle 0\left|\left[\exp\left[-\sum_q[\beta_{mq}(t)\hat{b}_q^\dagger(t) - \beta_{nq}^*(t)\hat{b}_q(t)]\right]\hat{a}_m(t)\hat{a}_n^\dagger(0)\right.\right.\right. \\ &\qquad \left.\left.\left.\times\exp\left[\sum_{q'}[\beta_{nq'}(0)\hat{b}_{q'}^\dagger(0) - \beta_{nq'}^*(0)\hat{b}_{q'}(0)]\right]\right]\right|0\right\rangle \ . \end{aligned} \quad (5.13)$$

Bearing in mind that (see BWL)

$$\hat{A}_m(t) = \hat{A}_m(0)e^{-i\Omega t}, \quad \Omega = -\sum_q \omega_q|\chi_q|^2 \ , \quad (5.14)$$

and combining it with (5.2a), we can write

$$\hat{a}_m(t) = \hat{a}_m(0)e^{-i\Omega t}\exp\left[\sum_q[\chi_m^q\hat{b}_q(0) - \chi_m^{*q}\hat{b}_q(0)]\right]\exp\left[-\sum_{q'}[\chi_m^{q'}\hat{b}_{q'}^\dagger(t) - \chi_m^{*q'}\hat{b}_{q'}(t)]\right] \ . \quad (5.15)$$

Using the properties of the coherent-state displacement operator (Appendix A, BWL), after substitution of (5.15) into (5.13), we obtain

$$\begin{aligned}\langle\phi_1(t)|\phi(t)\rangle = \sum_n P_n\exp\Bigg[& i\lambda(t) - i\Omega t - i\sum_q|\chi_q|^2\sin\omega_q t - i\sum_q \mathrm{Im}[\chi_n^q\beta_{nq}^*(0)(e^{i\omega_q t}-1)] \\ & - i\sum_q\mathrm{Im}\{\beta_{nq}(t)[\beta_{nq}^*(0)e^{i\omega_q t} - \chi_n^{*q}(1-e^{-i\omega_q t})]\} \\ & - \tfrac{1}{2}\sum_q|\beta_{nq}(t)e^{i\omega_q t} - \beta_{nq}(0) + \chi_n^q(e^{i\omega_q t}-1)|^2\Bigg] \ . \end{aligned} \quad (5.16)$$

Finally, introducing (5.10a) and (5.10c) into (5.16) we obtain

$$\langle \phi_1(t)|\phi(t)\rangle = 1 \ . \tag{5.17}$$

There is a major difference between our results and the results of BWL, because (5.11), (5.12), and (5.17) show that the dynamics of Davydov's function $|D_1(t)\rangle$ given by the ELE, for the most general initial conditions and $I=0$, is equivalent to the dynamics of the exact solution of the SE for the same initial conditions. It is also easy to show that the propagators are identical:

$$\langle \phi(0)|\phi(t)\rangle \equiv \langle \phi(0)|\phi_1(t)\rangle = \sum_n P_n e^{-i\Omega t} \sum_q (1-e^{-i\omega_q t})|\beta_{nq}(0)+\chi_n^q|^2 \ , \tag{5.18}$$

which implies that $|\phi_1(t)\rangle$ and $|\phi(t)\rangle$ generate the same optical spectrum. The final conclusion is that in the case $I=0$, $|D_1(t)\rangle$ describes the dynamics of the system exactly, as concluded previously from the general results of Sec. IV.

VI. CONCLUSION

In order to avoid a misunderstanding, we wish to conclude by clearly stating the results of this paper. We studied the system described by the Fröhlich Hamiltonian (1.1) and looked for the wave function in the form (2.1). We have shown that the wave function $|D_1(t)\rangle$ defined by (2.1), whose time dependence is determined by the coefficients $\psi_n(t)$ and $\beta_{nq}(t)$ satisfying the ELE's (which follow from the Langrangian of the system), does not satisfy the Schrödinger equation in the general case. In the particular case $I=0$, the Schrödinger equation is satisfied. The case $I\neq 0$, when $|D_1(t)\rangle$ becomes only an approximate solution will be discussed in a subsequent paper.

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